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Published in:
Solid State Communications

DOI:
10.1016/0038-1098(87)90269-9

Publication date:
1987

Solid State Communications, Vol.63,No.6, pp.451-456, 1987.
Printed in Great Britain.

0038-1098/87 $3.00 + .00
Pergamon Journals Ltd.

VALENCE FLUCTUATIONS IN $La_{2-x}Sr_xCuO_4$

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(received 24 April 1987 by S. Alexander)

Ab-initio electronic band structure calculations are presented for the perovskite La_2CuO_4 and for this material doped with Sr for a super-cell of composition $La_3SrCu_2O_8$. This material is close to the high Tc superconductor $La_{2-x}Sr_xCuO_4$ discovered recently. The Sr doping gives rise to strong valence fluctuations. We discuss the effect of the valence fluctuations on the stability of the lattice, indicating a small value of U and enhancing the electron-phonon coupling λ, mainly by a mechanism of incipient peroxide formation.

1. Introduction

One of the characteristic features of the recently discovered high-T_c superconductors [1,2,3] derived from the oxide La_2CuO_4 is the mixed valence of the copper constituent (Cu^{2+} and Cu^{3+}), which results from substituting a fraction of the trivalent La-ions by bivalent Ca, Ba or Sr dopants. A similar mixed valence is also found in the two previously discovered oxide superconductors $BaPb_{1-x}Bi_xO_3$ (Bi^{3+},Bi^{5+}) [4] and $Li_xTi_{2-x}O_4$ (Ti^{3+},Ti^{4+}) [5].

An important question is whether the mixed valence is static, namely certain Cu-sites are bivalent and others trivalent, or whether all the Cu sites are equivalent and have a dynamically fluctuating charge. To compare, in the monoclinic phase of $BaPb_{1-x}Bi_xO_3$ there are crystallographically inequivalent Bi-sites, and these have been interpreted as having different valence. However, infrared and X-ray photoemission spectroscopy [6] give no indication of a significant charge difference at these sites.

The nature and the role of the mixed valence of Cu in the new compounds have not been established. In most papers which has been circulating recently and which suggest a theoretical explanation, the only effect of the transforming some of the Cu^{2+} to Cu^{3+} is to suppress the tetragonal to orthorhombic transition leading to the semiconducting ground-state of La_2CuO_4. This is achieved by destroying the nesting required for a Peierls transition [7], by shifting the Fermi energy away from a Van-Hove singularity to avoid a band Jahn-Teller effect [8], by "melting" a resonating valence-bond ground-state [9], or by adding a bipolaron condensate to a commensurate charge density wave [10].

In the present study we demonstrate that the doping of the La_2CuO_4 compound produces dynamical valence-fluctuations on the Cu-sites and we propose that these charge fluctuations play an important role in the mechanism of superconductivity. Their effect is threefold: Their presence indicates a reduced Coulomb-repulsion; they lead to a strong electron-phonon coupling. The latter is due mainly to the incipient formation of dynamical peroxide coupling and also of an enhanced coupling strength to the breathing mode of the oxygens. Finally, the valence fluctuations suppress a coherent static deformation of the lattice, which is implied by a strong electron-phonon coupling.

2. Supercell Band Calculations

We report here calculations on a supercell of La_2CuO_4. The supercell approach allows the introduction of Sr without relying on the virtual crystal or CPA approximation. The method used was the recently developed LSW method, to be described elsewhere [11]. It is an all-electron self-consistent-field method employing exactly the same approximations as the more familiar ASW [7] and LMTO [8] methods.

We first calculated the undoped system La_2CuO_4. The results obtained were in excellent agreement with previous calculations [14,15] and will not be discussed here for that reason. In order to allow for the substitution of La by Sr we doubled the unit-cell by employing the primitive tetragonal unit-cell. This leads to a unit cell of composition $La_3SrCu_2O_8$. The direct consequence of the replacement of La by Sr is the reduction of symmetry leading to two inequivalent Cu atoms in the unit-cell. In this sense our calculations differs from calculations employing the virtual crystal approximation. The introduction of Sr reduces the number of valence electrons from 82 to 81. A rigid band model would lead to a lowering of the Fermi-energy and consequently an emptying of states of primarily Cu-d and O-p character and hence to an average smooth increase of the valence of Cu on all sites. In our calculations a different phenomenon happens. The introduction of Sr in fact introduces strong valence-fluctuations on

the copper-sites. The calculation oscillates indefinitely between the state in which Cu(1) has a low valence and Cu(2) has a high valence and the state in which the valences are reversed. Crucial for the occurrence of these oscillations is that one has allowed the system the necessary degrees of freedom, by treating the copper atoms inequivalent. Valence fluctuations like these have been observed in $PbTaS_2$, $SnTaS_2$ experimentally [16] as well as in band-structure calculations [17]. They are usually connected with a (formally) unstable valence connected with a non-negligible symmetry-breaking phenomenon. In this case this is accomplished by the substitution of La by Sr. The valence-fluctuations are so strong here that they prevented us from obtaining converged results in spite of the application of various type of mixing and using actual mixing as low as .003.

It is well-known that Cu is very sensitive to Jahn-Teller deformations and that Jahn-Teller deformations are sensitive to the valence of Cu [1]. The undoped system shows already an elongation of the Cu-O distances in the z-axis due to the JT-effect. Presuming that, conversely, the stability of the static occurrence of a Cu atom in a certain valence would be sensitive to JT-deformations, we attempted to help to converge the calculation by allowing additional JT distortions.

For one type of Cu the JT deformations were removed by shifting the Oxygens towards the Cu, for the other Cu the same displacement of O was introduced into the opposite direction. The resulting deformations are shown in Fig. 1. This calculation could be converged, The resulting Cu partial density-off states curves showed big differences as displayed in Fig. 2. Also a difference as big as .33 electron was found for the number of d electrons within identical Cu-spheres. It is an important question whether these differences, indicating different Cu valences, are due to the introduction of Sr or to the additional JT deformations necessary to converge the calculation. In order to investigate this question we performed a calculation on $La_4Cu_2O_8$ without Sr but with the same deformations of the oxygen-lattice as in the previous calculation. The calculation converged smoothly without any differences between the still inequivalent copper atoms whatsoever. We conclude that the partial substitution of La by Sr introduces strong valence-fluctuations on the copper-sites.

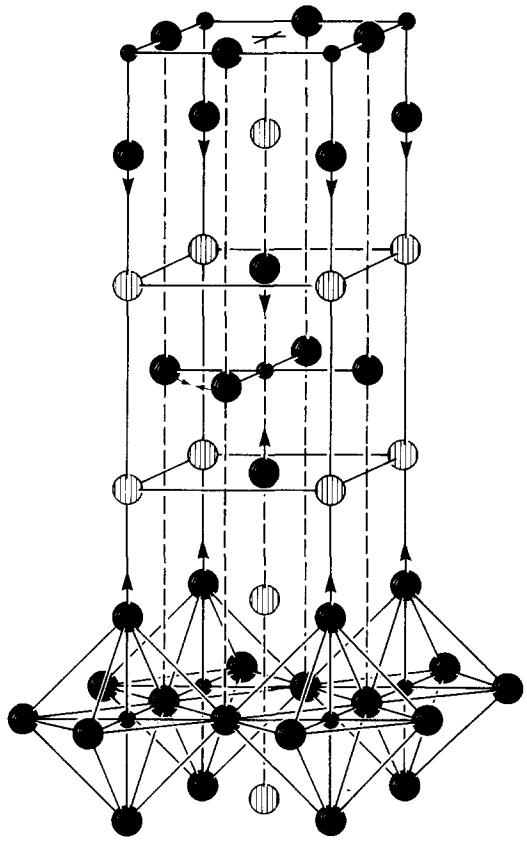

Fig. 1 Unit cell of La_2CuO_4. Bold arrows indicate additional Jahn-Teller defomations applied to converge the calculation on $La_3SrCu_2O_8$. Small arrows indicate the deformations taken into account in the calculation for the peroxide-mode. The latter calculation did not need the additional Jahn-Teller deformations.

3. The Electron-Phonon Coupling

We suggest that the pairing mechanism in the present compounds is provided by the coupling to the orthorhombic distortion mode and the breathing mode. In the first case the distance between the two neighbouring oxygens is modulated, and as they approach each other there is an incipient peroxide formation. It is difficult to estimate at this stage which of these two modes plays a more important role, but we can argue that both couple strongly to the electronic motion and that this coupling strength is a direct consequence of the valence fluctuations. Let us now discuss the two cases separately.

3a. The Dynamic Peroxide Coupling.

The electronic structure of compounds consisting of metals and group VI elements can be described usually in terms of a filled, broad anion band and narrow transition-metal d states, with some degree of hybridization. The position of the metal-d states is usually above the anion valence-band, although some filled d-states frequently overlap the valence-band. The position of the d-states with respect to the valence-band is determined by the electronegativity of the metal and its valence in the compound of interest. The deepest levels are found for noble metals in a high valence-state. In such a case it can happen that empty d-levels start to overlap the anion valence-band. This process leads to the creation of holes in this anion-valence-band. A too large concentration of holes in the valence-band is found to be always unstable, however. Energy can be gained by pairing the anions. This leads to the splitting-off of an antibonding anion subband above E_f and a subsequent reduction of

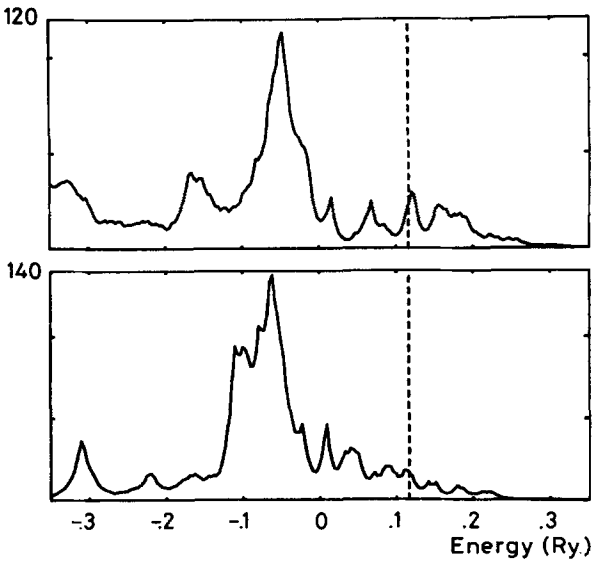

Fig. 2 Partial density of states curves for the two inequivalent copper atoms in the unit-cell in the case of $La_3SrCu_2O_8$ (smoothed with a Gaussian, FWHM = .1 eV).

the valences of both the anion and the metal. Further consequences are the lifting of the anion-p transition-metal-d degeneracy at the Fermi level and the restoration of an ionic-like picture with the anions replaced by covalently bonded anion-pairs. It is exactly this phenomenon which is responsible for the occurrence of the pyrite, the marcasite and the peroxide-structures [18]. The pyrite-structure, for example, is simply the NaCl structure with the anion-positions occupied by anion-pairs. Of importance here too is the structure of Calaverite, $AuTe_2$. In $AuTe_2$, with formally gold in its tetravalent state, the tendency to pair the anions leads to an incommensurate modulation of the anion lattice. The reduction of the valences ($2Te^{2-}$ to $Te_2)^{2-}$) leaves Au in its divalent state, which - as a classical example of a negative U case - leads to a charge separation into Au^+ and Au^{3+}. This theoretical prediction [19] enabled the determination of the crystal structure [20].

A similar situation occurs in the case $La_{2-x}Sr_xCuO_4$. The valence fluctuations introduced by Sr lead to a Cu^{3+} state, which is not stable with respect to deformations of the anion-lattice. The difference from the calaverite case is that the situation here is not static but since the valences fluctuate dynamically, they lead to a dynamic coupling between the copper-d electrons and deformations of the anion-lattice towards pair-formations. This situation is exactly found in a calculation on $La_3SrCu_2O_4$ with the required deformation of the anion lattice. These deformations are shown in Fig. 1. The occurrence of the dynamic peroxide formation has the following consequences.

1) A net charge transfer from oxygen to copper takes place. As a consequence the differences between the two copper-atoms are strongly reduced. The difference in d-electrons within identical spheres is reduced from .33 to .07 electrons.
2) It induces a split-off peak of primarily oxygen-p character just above E_f. This peak should be observable in BIS or X-ray absorption spectroscopy.
3) It leads to an asymmetrical broadening of the oxygen 2s states towards higher binding-energy [18], which should be observable in photoemission spectroscopy. The effect is however greatly diminished compared with static peroxides or pyrites since the oxygens are in the peroxide-state only a fraction of the time.

The peroxide formation modulates the charge on the vibrating (O-O) pair, and this modulation contributes to the electron-phonon coupling λ. This contribution can be estimated from

$$\lambda_{per} = \frac{1}{2} p (M\omega_{ph}^2)\left(\frac{\partial R}{\partial n}\right)^2 n(E_F) \qquad (1)$$

where R is the oxygen-oxygen distance, n is the charge on the O_2 "molecule", M is the oxygen mass, ω_{ph} is the peroxide vibration frequency and p=2 for the two (O-O) pairs of one Cu. This formula was applied to organic metals [21] like TTF-TCNQ and an experimental determination of λ for the C≡N bond (for example) gives a value approximately 30% lower than this theoretical estimate [22]. Unfortunately, we cannot estimate the energy associated with the dynamic peroxide formation mode, as the calculation of the undistorted case was impossible without the introduction of additional Jahn-Teller deformations. Therefore, we cannot give at present a reliable estimate of this contribution to λ except for stating that the present band calculation indicates that it is large.

3b. The Breathing-mode coupling.

To estimate the coupling strength to the breathing-mode we use again eq(1), where now R is the Cu-O distance and the factor p=4 represents the four Cu-O bonds. The Cu-O distance in La_2CuO_4 (namely for Cu^{2+}) is R=1.9 A. Comparison with the Cu-O distance in other copper-oxides [23] reveals a change of δR=.25 A for a change of one valence electron. Assuming [24] ω_{ph}=60 meV and $N(E_f)$=1.5 eV^{-1} one finds $\lambda \tilde{} 2$.

This estimate depends essentially on the ability of the CuO_4 complex to gain or lose charge as the Cu-O distance changes. Imposing a restriction that the charge on the CuO_4 complex remains constant leads to a significant smaller value of λ. Benneman and Freeman [25] estimate a value of $\lambda \tilde{} .5$.

Another factor which may cause a larger value of λ (for all modes) is the 2d-nature of the electronic structure. In this case the Fermi energy may lie in the neighbourhood of a Van Hove singularity in the density of states [8],

giving rise to an enhanced $n(E_f)$ and thus to a larger λ.

In conclusion, a total value of λ in the range 2-4 appears reasonable.

4. The Relevant Time Scales and Lattice Instability

For λ as high as estimated above one expects the formation of bipolarons [26]. All materials in which the existence of bipolarons has been established experimentally have an insulating ground-state [27]. Nevertheless, in principle bipolarons may also condensate into a superconducting state [28]. However, we want to suggest here another possibility invoking again the fluctuating charge on the Cu sites. If the period of these fluctuations τ_{vf} is smaller or of the order of the characteristic time for a lattice-distortion associated with the formation of bipolarons, then the system (above the superconducting transition temperature T_c) will remain an ordinary metal with a high value of λ. We shall now attempt to estimate the times involved. When the valence of copper changes by 1 (between +3 and +2) the Cu-O distance for the 4 oxygen neighbors in the plane changes by approximately $\delta R = .25$ A; the amplitude of the zero-point vibrations for the breathing-mode with a frequency of 60 meV is approximately $\langle \delta r \rangle^2 \simeq .03$ A. Thus the change can be characterized by $\delta R^2/\langle \delta r \rangle^2 \simeq 60$ phonons that must be dissipated. The question is what is the relaxation-time required for a lattice instability to develop due to the large electron-phonon coupling constant λ associated with these modes. The dissipation of the phonons may take place by emission into the phonon-band of the solid, and/or conversion to the various internal or rotational modes of the CuO_4 complex. For a molecule (the size of benzene or anthracene) in an inert medium, the relaxation rate is given by the formula:

$$W = \frac{C^2 \sqrt{4\pi}}{\sqrt{E_m h\omega}} \exp(-2E_A/h\omega) \qquad (2)$$

(4.10) of ref. [29] ω is the phonon-frequency, here about 60 meV. E_A is the difference in energy between the two states. C and E_m are typical electronic energies. C is in effect the electronic transfer integral in the case of complete overlap of the atomic positions in the two different states. For the case of a 2d cosine band $E(\vec{k}) = 2C(\cos k_x a + \cos k_y a)$, $C = 1/4$ of the bandwidth. If the bandwidth of an individual copper 3d subband is 1 eV., than $C \simeq 1/4$ eV. E_m is the energy needed to distort the CuO_4 complex from the value appropriate for divalent copper to a value appropriate for a valence $2+\delta$ (Fig. 3). For trivalent copper $\delta = 1$ and $E_m \simeq 5$ eV. For a valence of 2.5, $E_m \simeq 1.25$ eV. E_A is most difficult to estimate. If we assume tentatively that $E_A \simeq .2$eV, then $W \simeq 2.5$ meV. However, because of the uncertainty in the various parameters, in particular in the value of E_A, this is at best an order-of-magnitude estimate. Still, we see that it is plausible that W is one or two orders smaller than ω.

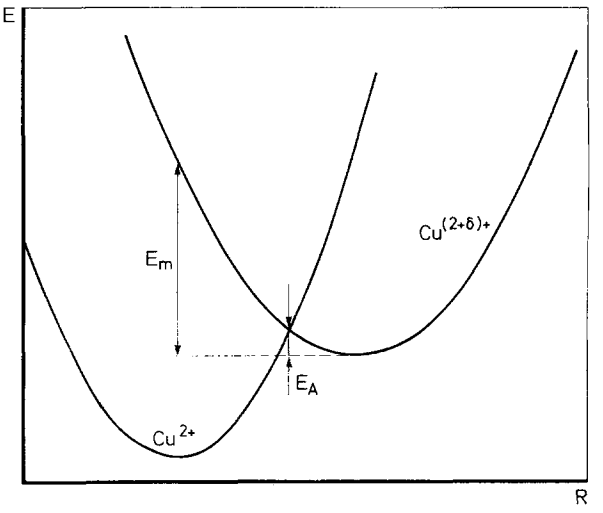

Fig. 3 Schematic diagram for the total energy as a function of Cu-O distances. The quantities in the figure are explained in the text.

When the valence-fluctuation-time τ_{vf} is shorter than, or of the order of W^{-1}, the system cannot relax and the instability expected because of the large value of λ cannot take place. If τ_{vf} is longer than W^{-1}, the valence fluctuation process is adiabatic, and a lattice distortion, or bipolaron formation, is possible.

In contrast, when τ_{vf} is longer than the characteristic time for superconductivity, which may be (2δ)sup-1 or ω_{ph}^{-1} (both 2δ and ω_{ph} are of the order 20-60 meV), the valence fluctuation does not interrupt the interactions responsible for superconductivity.

Thus we have an appreciable interval:

$$(2 \text{ meV} \simeq) \; W < \tau_{vf}^{-1} < 2\Delta \; , \; \omega_{ph} \; (\simeq 50 \text{ meV}) \qquad (3)$$

for which the valence-fluctuations prevent a lattice-instability (due to strong electron-phonon coupling), yet do not interfere with the superconductivity.

5. The Coulomb Interaction

In the present study we have related the basic features of the superconducting compounds based on La_2CuO_4 to the strong valence fluctuations of the doped materials. These fluctuations have been demonstrated in a supercell bandstructure calculation and cannot be seen in a more traditional single-cell method with a virtual-crystal approximation. The presence of these fluctuations indicates a strong reduction in the Coulomb repulsion between d-electrons on the Cu-sites. It is the size of U which prevents such fluctuations in

ordinary metals. On the other hand, a negative U usually leads to mixed valence systems accompanied by lattice-deformations (Pb_2O_3, Fe_2O_3, Pb_3O_4, etc.). Thus, the presence of valence fluctuations indicates the intermediate case of a small but positive U. It is exactly this coulomb-repulsion which has to be compensated by pairing mechanisms like electron-phonon interaction in order to lead to a superconductive state. We have suggested that these valence-fluctuations may lead to a value of λ, McMillan's formula for T_c is not valid and the transition temperature is determined [30,31] by:

$$T_c = .18 \langle\omega^2\rangle^{1/2} \lambda^{1/2}. \qquad (4)$$

The crossover to this expression occurs at $\lambda=.8\omega^2_{max}/\langle\omega^2\rangle$. In this range of λ, the effect of the Coulomb interaction is stronger [13] than given by McMillan's formula, and:

$$\lambda_{eff} \tilde{=} \lambda(1 + 2.6\mu^*)^{-1} \qquad (5)$$

(and not $\lambda_{eff} = \lambda-\mu^*$). Moreover, if the phonons involved have a high frequency, then $\mu^*=\mu/(1+\mu\ell n\ E_f/\omega_{ph})$ is not so reduced [32] with respect to μ (because of the second factor in the denominator is smaller). For these two reasons, even a moderate value of U has a drastic effect on T_c. However, as we have seen above, μ itself is small, therefore μ^* is also small.

6. Conclusions

We have shown by ab-initio computer calculations that the doping of La_2CuO_4 with Sr gives rise to very strong valence-fluctuations. These valence fluctuations play an essential role for the superconductivity in several respects:

1) They prevent lattice instabilities, as well as polaron and bipolaron formation, that would otherwise take place because of the large value of λ.
2) They indicate a small value of U (and thus of μ), which is: vital for a high T_c.
3) They increase the value of λ, since the phonons are essentially associated with changes of the charge on the oxygen atoms (due to the incipient peroxide formation) and the Cu-O bonds.
4) Independently of the above, the dynamic peroxide formation leads to the pairing of hole-states and thus in principle provides a mechanism by itself which could contribute to the superconductive properties. We will address this point in the near future.

Acknowledgement
Extensive discussions with A.R. Williams in all stages of this work are greatfully acknowledged. Part of this research was supported by the Stichting voor fundamenteel onderzoek der materie (FOM).

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